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SYNTHESIS OF CERAMIC PIGMENTS WITH MERWINITE CRYSTAL STRUCTURE

I. V. Pishch,[1,3] G. N. Maslennikova,[2] and N. A. Gvozdeva[1]

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The results of a study of the possibility of synthesizing pigments based on merwinite are presented, methods for directed regulation of structure and phase formation processes for synthesis of pigments possessing high physical-chemical properties are developed and a relation is established between the temperature–time parameters of synthesis, the content of the added chromaphoric oxides with the type and amount of color-carrying phases giving saturated colors and a wide range of pigment colors.

Key words: pigments, chromaphore, mineralizer, crystal structure, merwinite.

Construction ceramic imitating the structure of natural granite can now be produced. Such materials possess good decorative characteristics and are distinguished by high physical-mechanical properties. Ceramic granite is obtained using heat-resistant pigments to color the ceramic tile mix. For this reason the production of high-temperature pigments with a wide color range for volume coloring based on readily available materials is a promising direction of research.

Ceramic heat-resistant pigments comprise colored metal oxides and their combinations, silicates of the type spinels, merwinite, garnets and so forth. The color of pigments is obtained by incorporating in acceptor crystal lattices transition-metal ions (Cr^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+} and others) and is due to light absorption as a result of $d – d$ electron transitions or charge transfer [1, 2].

The high-temperature phase of merwinite $MgO \cdot 3CaO \cdot SiO_2$, formed in the ternary system $CaO–MgO–SiO_2$, is a favorable acceptor crystal lattice for synthesizing ceramic pigments. Merwinite is characterized by a perovskite structure with large cells. It melts incongruently at 1575°C, decomposing into $2CaO \cdot SiO_2$, periclase and a liquid. In [3] it is shown that merwinite can be synthesized from the pure oxides CaO, MgO and SiO_2 using B_2O_3 as a mineralizer as well as from calcium orthosilicate and periclase. Multicolored pigments are obtained by isomorphic substitution of the ions Ca^{2+}, Mg^{2+} and the coloring oxides Co^{2+}, Ni^{2+}, Fe^{3+} and Cr^{3+}.

Transition 3*d* elements enter the crystal lattice of the ions listed above by means of solid-phase reactions at temperatures 1200 – 1300°C in the presence of mineralizers. The insertion of mineralizing additives makes it possible to lower the synthesis temperature.

Mineralizers have a strong effect on the crystal lattice of the sintered material as well as on the color of the synthesized pigments. The effect of the mineralizers is to form a liquid phase, which loosens the crystal structure, putting it into an active state, and to increase the contact surface area between the reagents as well as to increase the diffusion rate. To intensify many reactions in the solid phase the content of a mineralizer additive must not exceed 1 – 5%[4] of the amount of the overall mixture.

The objective of the present work was to develop methods of controlled regulation of structure and phase formation processes for the purpose of synthesizing pigments with the crystal structure of merwinite, which possess a high coefficient of light reflection and enhanced heat and chemical resistance, and to determine the relation between the temperature–time parameters of synthesis, the content of the chromaphoric oxide additives and the mineralizer with the type and amount of the light-carrying phases which are formed and give saturated colors and a wide color range for the pigments.

The pigments were synthesized from magnesite (Satkinskoe deposit in Russia) and chalk (deposit in the Kolyadichi Volkovysskii Rayon, Belarus). In addition, the following components were added to the mix: H_3BO_3 as the

[1] Belorussian State Technological University, Minsk, Belarus.
[2] State University of Management, Moscow, Russia.
[3] E-mail: root@bstu.unibel.by.

[4] The content of the components by weight, wt.%, is presented here and below.

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mineralizer and chromaphoric oxides (CoO, NiO, Fe_2O_3, Cr_2O_3). In previous studies the mineralizer was introduced into the mix in the amount 2.5% above 100% [3].

The powders of the initial components were carefully and conjointly comminuted and mixed. The prepared samples were kilned in an electric furnace at temperatures 1000, 1100 and 1200°C with 1 h soaking at the highest temperature. To widen the color range of the pigments the possibility of partial and complete substitution of 3*d* transition metal oxides for CaO and MgO in the merwinite structure was investigated.

Pigments with a wide color range, depending on the type of chromaphoric oxide used, were synthesized: light-green, green, brown, blue, light-blue and violet colors. The synthesized ceramic pigments are characterized by a single-tone, bright and saturated coloration. The pigments kilned at 1000°C possess weak low chromaphoric properties, indicating that their content of the color-carrying phase is too low. It was determined that the optimal synthesis temperature is 1200°C.

Pigments with color varying from light to dark violet were obtained by substituting CoO for CaO. Similar changes in the coloration of pigments were also obtained by substituting Co^{2+} for Mg^{2+}. It was found that green pigments were synthesized by using the oxide NiO. The color changed from light-green to green and dark-green by substituting NiO for CaO.

Differential thermal analysis was used to determine the thermal effects of the solid-phase reactions occurring. The presence of two endo effects associated with the decomposition of magnesium carbonate (580°C) and calcium carbonate (820°C) is observed in the initial state. Calcium metasilicate, which is stable at low temperatures and decomposes at 1020°C, is observed to form after partial decomposition of calcium carbonate at 650°C. With partial substitution of CoO for CaO the curve remains similar with no significant changes. However, the heat effects are shifted to higher temperatures. Actually, the exo effect at 750°C corresponds to the formation of calcium metasilicate and its decomposition at 1020°C.

X-ray phase analysis established that the main crystal phases are merwinite, diopside, forsterite and calcium silicate. Diffraction peaks belonging to merwinite as well as CoO, CaO and MgO (0.143, 0.171, 0.212, 0.241 and 0.275 nm) appear when CoO is substituted for CaO. The presence of α-quartz (0.182, 0.309 and 0.398 nm) is observed, which attests the incompletion of phase-formation processes.

When NiO is introduced (partial substitution for CaO) diffraction peaks characteristic for NiO appear (0.147, 0.208, 0.225, 0.24 nm). In addition, the crystalline phase of diopside (0.292, 0.297, 0.321 nm) and small quantities of merwinite are clearly recorded.

The amount of merwinite increases when Ni^{2+} replaces Mg^{2+}. This is because the ionic radii of these ions are close, so that Ni^{2+} can enter into the merwinite structure.

TABLE 1. Color Characteristics of the Optimal Compositions of Pigments

Oxides of 3*d* transition metals	Color coordinates		Dominant wavelength, nm	Tonal purity, %
	x	*y*		
CoO	0.129	0.197	480	45
Cr_2O_3	0.243	0.573	530	38
Fe_2O_3	0.523	0.349	586	30
NiO	0.311	0.479	558	37

Iron orthosilicate (0.146, 0.181, 0.21, 0.245, 0.32 nm) appears when Fe_2O_3 partially substitutes for MgO. However, the introduction Fe_2O_3 into the mixes destroys the merwinite crystal structure and gives rise to the formation of forsterite and diopside.

To study the chromaphoric properties the spectral reflection curves were obtained with a SF-18 spectrophotometer, which automatically recorded the reflection spectra in the wavelength range 400 – 750 nm.

The reflection coefficient and the color characteristics of the synthesized pigments with optimal compositions were determined in the course of the experiments; see Table 1. The dominant wavelength on the spectral reflection curves of pigments containing the oxide Cr_2O_3 lies in the range 500 – 530 nm, which corresponds to the green region of the spectrum.

The spectral reflection curves of iron-containing pigments are characterized by the presence of a peak in the region 580 – 590 nm. The spectral reflection coefficients of cobalt-containing pigments increase in the region 470 – 487 nm, which lies in the blue–light-blue range. The pigments synthesized using nickel oxide are characterized by a dominant wavelength lying in the region 558 – 562 nm. The color range of pigments synthesized using the oxide Fe_2O_3 is light-brown with the absorption curve peaking in the range 580 – 590 nm.

The nickel-containing pigments were found to have quite high reflection coefficients (80 – 90%). This corresponds to light, low-saturation tones. The introduction of cobalt oxide in the amount 5% into the initial composition led to the formation of pigments with a wide color range — from pale–light-blue to blue-black color, which is due to the coordination ion Co^{2+}. The blue and light-blue colors of the cobalt-containing pigments obtained are probably due to the tetrahedral coordination of the cobalt ions.

The pigments whose color is due to nickel oxide (II) are characterized by a light-green color, which changes to saturated light-green as the synthesis temperature increases. This coloration of the synthesized nickel-containing pigments is probably due to the tetrahedral coordination of the nickel ion (II) and is explained by absorption associated with charge transfer.

CONCLUSIONS

1. The relation between the temperature–time parameters of synthesis, the content of the chromaphores introduced, the amount of the crystal phases formed and the color characteristics of the pigments studied was established. The major crystalline phases were found to be merwinite, diopside, forsterite, calcium silicate and periclase as well as the oxides of 3*d* transition elements.

2. Pigments with a wide color range were obtained — light-green, green, brown, blue, light-blue and violet. The color of the pigments depends on the type and amount of the chromaphores used. The optimal compositions with tonal purity 30 – 45%, heat-resistance > 1100°C and acid-resistance 96.0 and 98.0% with respect to a 1 N solution of HCl were determined.

3. Industrial tests performed at Keramin, JSC gave positive results. The pigments of the compositions developed can be recommended for coloring glazes, ceramic mixes and engobes.

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